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Some New Concepts in the Stabilisation of Polymers

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Recent research has shown that a variety of antioxidants have the ability to trap alkyl radicals under conditions of rapid radical generation and/or low oxygen pressure [chain-breaking acceptor (CB-A) process]. When the antioxidant has a well characterised oxidised and reduced form, the resulting redox couple may give rise to a catalytic antioxidant effect under certain conditions. Such a CB-A/CB-D catalytic effect has been known to operate in polypropylene during processing and in rubber during fatiguing. It is also believed to account for the high fatigue resistance of sulphur vulcanisates.

The Chain-breaking Mechanism of Antioxidant Action

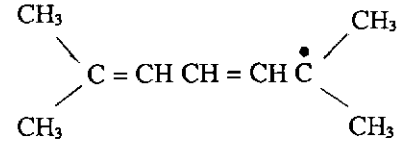
The classical theory of radical chain anti-oxidation, represented in its simplest form by *Reactions 1-4* suggests that the most important mechanism by which the kinetic chain reaction, *Reactions 2* and *3*, is terminated is by reduction of the alkylperoxyl radical to hydroperoxide by *Reactions 5* and *6* [the chain-breaking donor (CB-D) mechanism]:

	Initiation		
RH	$\rightarrow$	$R^\bullet$	...1
	Fast		
$R^\bullet + O_2$	$\rightarrow$	$RO_2^\bullet$	...2
	Slow		
$RO_2^\bullet + RH$	$\rightarrow$	$ROOH + R^\bullet$	...3
$2ROO^\bullet$	$\rightarrow$	Inert products	...4
$ROO + AH$	$\rightarrow$	$ROOH + A^\bullet$	...5
$A^\bullet$	$\rightarrow$	Dimers, *etc.*	...6

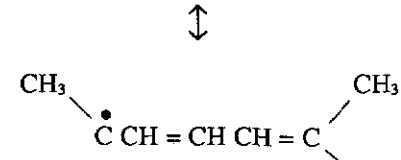
This mechanism which was originally proposed by Lowry[3] and subsequently elaborated by Bolland and co-workers[4,5] explains many antioxidant processes in liquid substrates at ambient oxygen pressures[6]. However, Bateman[7] in an elegant study of the effect of oxygen pressure on the termination reaction showed that in liquid hydrocarbons such as linoleic esters at low oxygen pressure, *Reaction 7* and even *Reaction 8* may be more important than *Reaction 4:*

$R^\bullet + ROO^\bullet$	$\rightarrow$	ROOR	...7
$2R^\bullet$	$\rightarrow$	R–R	...8

Reactions 7 and *8* become increasingly important when the alkyl radical R· is tertiary or is stabilised by electron delocalisation, e.g. in the alkenyl radical (I)[7]:



Ia



Ib

It has been known for many years that some oxidising agents can also be antioxidants[7] and in particular, quinones have been shown to be anti-fatigue agents in rubbers[8]. No entirely satisfactory explanation has been advanced to explain this observation. More recently,

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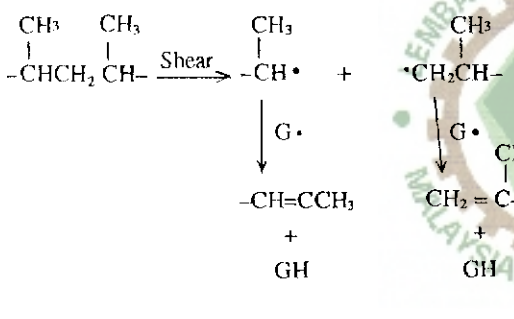
Henman[9] has shown that some oxidation products of the phenolic antioxidant BHT(I) are much more effective than the parent phenol as processing antioxidants for polypropylene. The quinonoid compounds II – IV *(Table 1)* are all formed from BHT under autoxidising conditions and it can be seen that all are much more effective than BHT itself.

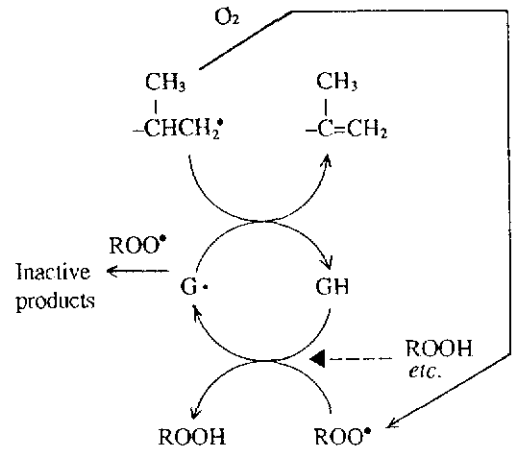
Chain-breaking Acceptor (CB-A) Antioxidants

The essential difference between the conditions to which a polymer is subjected during processing and during accelerated heat ageing is that during processing a) the polymer is subjected to high mechanical strain (shear) which leads to scission of a small proportion of the polymer chains, and b) air is deliberately excluded to avoid undue oxidation. Both of these conditions favour termination through alkyl radicals and in a more detailed study of the chemical transformations occurring with one of the above antioxidants, galvinoxyl, (II) Bagheri *et al.* [10,11] observed that galvinoxyl, G·, was substantially reduced to the corresponding phenol during the initial period when the shear in an internal mixer was highest. It was concluded that this was due to oxidation of macroalkyl radicals by galvinoxyl *(Scheme 1)* and indeed it was found that as G· disappeared from the system, GII(V) was formed almost quantitatively *(Figure 1)*, together with olefinic unsaturation *(Figure 2)*. However, a surprising feature was the subsequent partial regeneration of G· and the reciprocal disappearance of hydrogalvinoxyl (GH). This suggested that the oxidised and reduced forms of the antioxidant are both relatively stable and are capable of deactivating whichever of the chain propagating radicals is present in highest concentration in the system. This amounts to a catalytic antioxidant process *(Scheme 2)* and by chemical measurement of the unsaturation formed in the polymer it was concluded that one galvinoxyl radical is able to deactivate approximately fifty radicals in the polymer melt before it is destroyed by oxidation *(Reaction 9)* and the normal propagation process involving oxygen intervenes:



Scheme 1

The chain-breaking acceptor (CB-A) antioxidant mechanism



Scheme 2

Catalytic mechanism of galvinoxyl (G·)

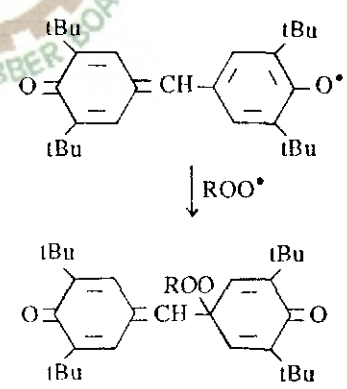


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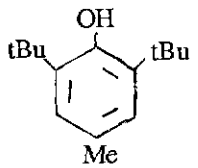
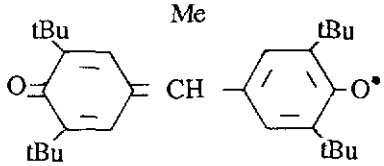
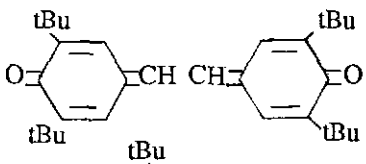
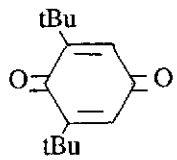
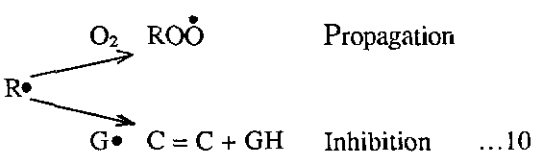
TABLE 1. MECHANO-ANTIOXIDANT EFFECTIVENESS OF BHT TRANSFORMATION PRODUCTS IN POLYPROPYLENE DURING PROCESSING

BHT transformation product		ΔMFI (m.mol kg^{-1}) 4.5	0.5
	I, BHT	100	270
	II, G·	45	45
	III, SQ	50	60
	IV, BQ	55	65

An interesting consequence of the above complementary oscillation of the concentration of oxidised and reduced species during the processing operation is that the heat ageing activity of the antioxidant depends on processing time[12]. The stability of the polymer is linearly related to the concentration of GH after processing. It therefore also oscillates with processing time. From this, it can be concluded that G· itself has relatively poor thermal antioxidant activity and that the CB-D antioxidant process due to GH predominates. The most likely reason for this is that G· cannot compete with oxygen for alkyl radicals when the latter is present in large excess in polypropylene *(Reaction 10)*:



It may also be destroyed directly by oxygen.

Nitroxyl Radicals as Catalytic Antioxidants

Other redox systems with stable oxidised and reduced states can act as melt stabilisers for polyolefins during processing[13]. *Table 2* shows that the inorganic redox systems, Cu^{2+} / Cu^{+} and $I^{\cdot}/I^{-}$ are effective processing stabilisers. They have limited practical utility, however, since the former is a powerful catalyst for oxidation of polymers under oven-ageing conditions (copper ions catalyse the radical decomposition of hydroperoxides and I_2 and HI are readily lost by volatilisation). However, CuI is an effective thermal antioxidant for polyamides and it seems likely that both the copper and the iodine are participating as catalytic chain-breaking antioxidants in this system. Nitroxyl radicals are much more important catalytic antioxidants in polymers[13,14]. Not only are they effective melt stabilisers for polypropylene[13-17] *(Table 2)* but they are also photo-antioxidants[14,16] and the aromatic nitroxyls are anti-fatigue agents for

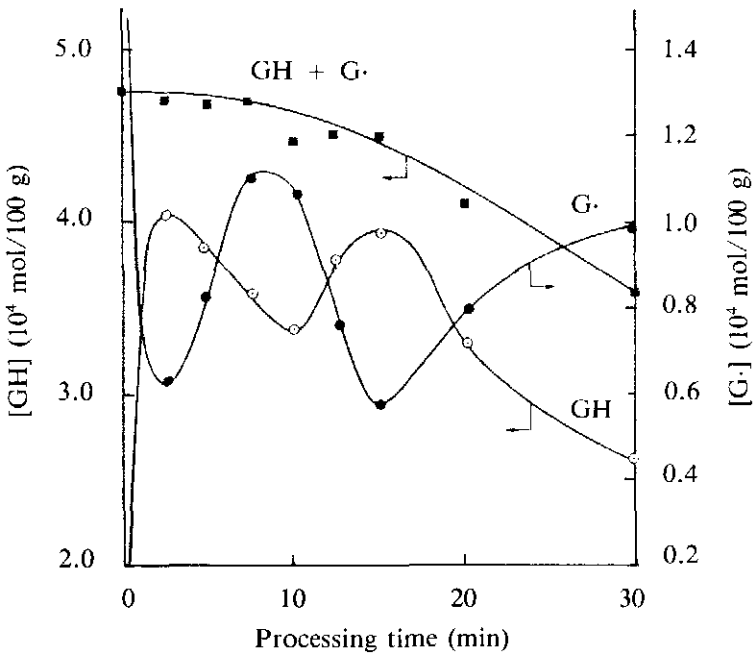


Figure 1. Changes in G· and GH concentrations in polypropylene during processing at 200°C. Initial G· = 4.74 × 10 $^{-4}$ mol/100 g. (After References 10 and 11)

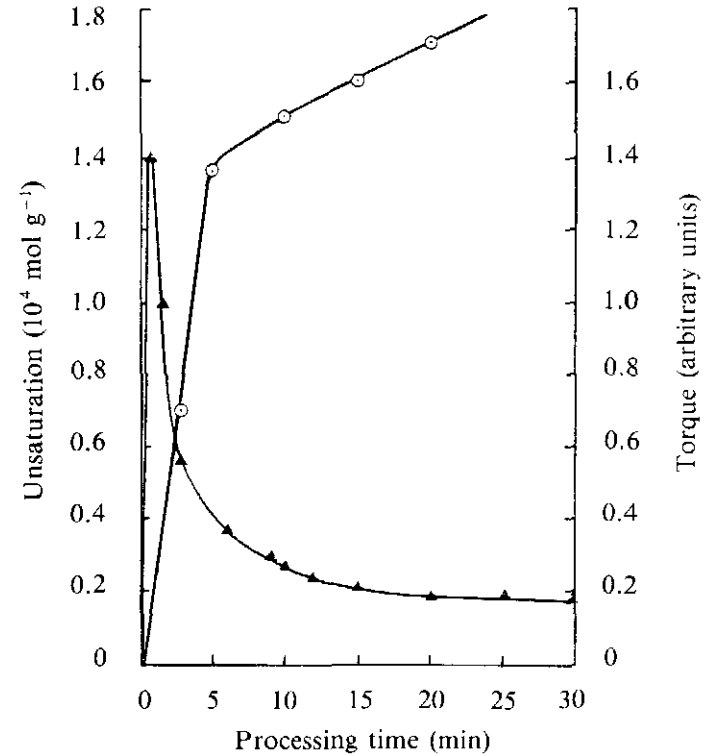
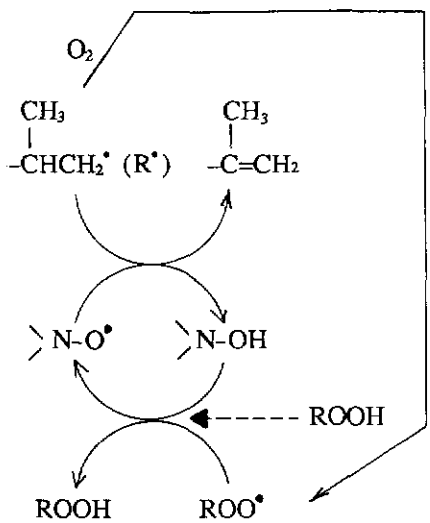


Figure 2. Relationship between the formation of unsaturation and the applied torque during processing of polypropylene at 200°C. Initial G· = 4.75 × 10^{-4} mol/100 g. (After References 10 and 11)

natural rubber[14,18]. Hindered piperidinoxyls (e.g. VI) undergo the same kind of complementary oscillation reactions with the conjugate hydroxylamine in polypropylene as does galvinoxyl *(Scheme 3)*[13-17]



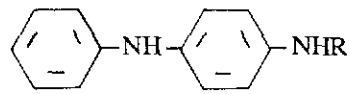
Scheme 3

Catalytic mechano-antioxidant activity of nitroxyls

and again the nitroxyl is ineffective in the presence of excess air[16]. The oscillatory cycle can be reproduced by computer simulation by introducing the appropriate rate constants for the individual steps and assuming a low rate of oxygen ingress to the mixer[13]. *Table 2* shows that the aromatic nitroxyls (VII) are also effective melt stabilisers for polypropylene and a study of a variety of nitroxyls in model systems by Berger and co-workers[19] has shown that they all have catalytic activity, their effectiveness depending on the structure of the autoxidising medium. In general, the more oxidisable the substrate, the higher is the stoichiometric inhibition coefficient f^*, in the system.

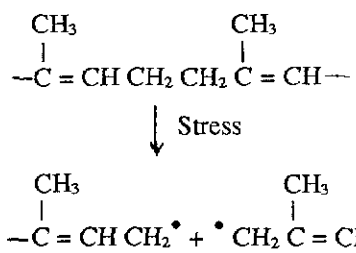
Nitroxyl Radicals as Anti-fatigue Agents for Rubbers

Aromatic p-phenylene diamines (VIII) are the longest established and most widely used



VIII

class of antioxidants in vulcanised rubbers. Their success derives from the fact that they are not only heat ageing antioxidants but they are also effective anti-fatigue agents and anti-ozonants[20]. The reason for their almost unique activity under conditions of mechanical stress has been in the past a cause of considerable puzzlement to antioxidant chemists, although it has been recognised that fatigue differs from thermal oxidation processes in that a small but mechanically significant number of rubber chains are subjected to stresses in excess of those required to break carbon-carbon bonds in the polymer backbone[21,22] *(Reaction 11)*. This gives rise to macroalkyl radicals in the polymer substrate:



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Under conditions of oxygen saturation the macroalkyl groups produced in *Reaction 11* will be converted rapidly to alkylperoxyl, *Reaction 12* and then to hydroperoxides

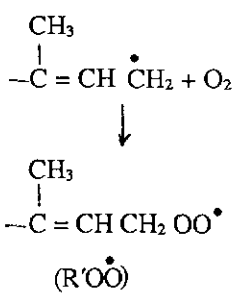

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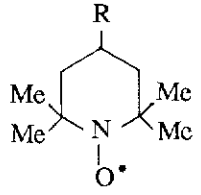
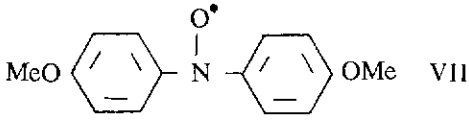
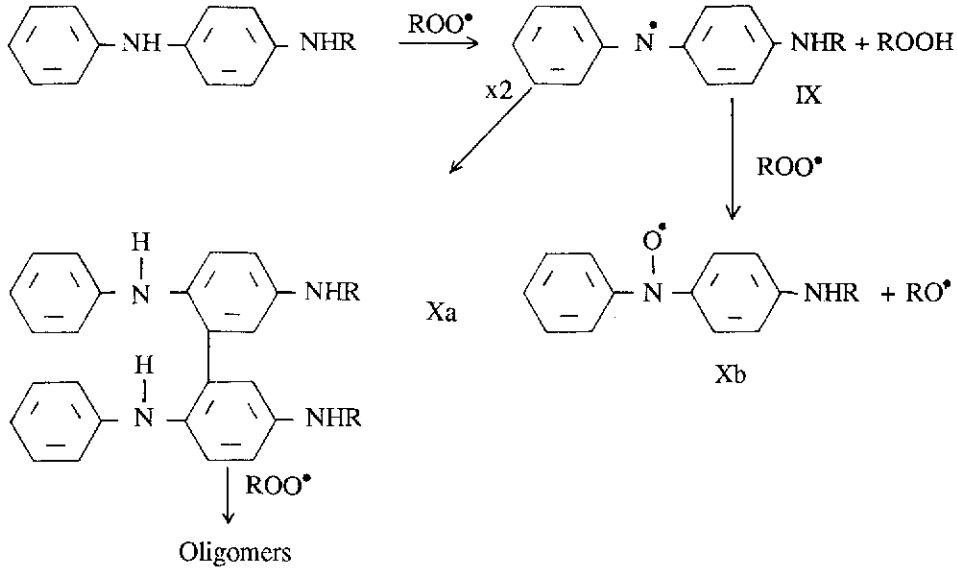
TABLE 2. REDOX SYSTEMS AS MECHANO-ANTIOXIDANTS FOR POLYPROPYLENE DURING PROCESSING[13]

CB-A	CB-D	MFI (m.mol kg^{-1}) 4.5	0.5
I$^{\bullet}$	HI	45	50
Cu^{2+}	Cu^{+}	40	80
 VI	>N–OH	–	55
 VII	>N–OH	–	45
BHT		100	270

by the parent amine *(Scheme 4)*. The resulting arylaminyl radicals, IX, are highly reactive and can undergo two alternative reactions giving either oligomers (e.g. Xa,



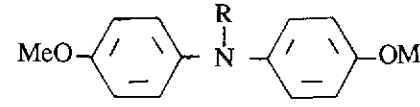
Scheme 4

Alternative transformation products of N-alkyl-p-phenylene diamines in the presence of alkylperoxyl radicals

Scheme 4) or the corresponding nitroxyl radical (Xb)[23].

Katbab and Scott[24] studied the formation of radicals in vulcanised NR by ESR. Both alkylperoxyl radicals and nitroxyl radicals are formed rapidly under dynamic stress in a Monsanto fatigue to failure tester *(Figure 3)*. The peak in the alkylperoxyl concentration occurs before substantial amounts of nitroxyl are present, confirming the sequence of events given in *Scheme 4*. The nitroxyl concentration also goes through a maximum, decaying away to a stationary state.

If, instead of arylamine, a nitroxyl (XI, R = O·) was used, this was substantially unreacted after compounding but after vulcanisation only about 1% could be detected[25]. The remainder was transformed to a mixture of the free hydroxylamine, XI, R = OH and the parent amine (XI, R = H):



XI

The nitroxyl concentration in the rubber remained sensibly constant during fatiguing but only a small fraction of nitroxyl originally added could be measured until the failure of the rubber sample, when it increased rapidly and the arylamine and hydroxylamine concentrations decayed. It appears then that the amine (XI, R = H), the nitroxyl (XI, R = O·) and the hydroxylamines, XI, R = OH and R = OP (where P is the polymer)

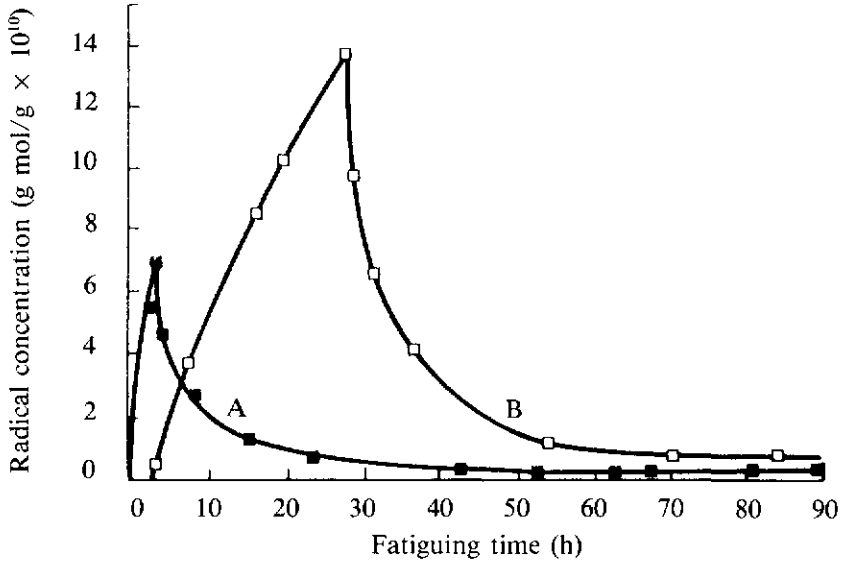
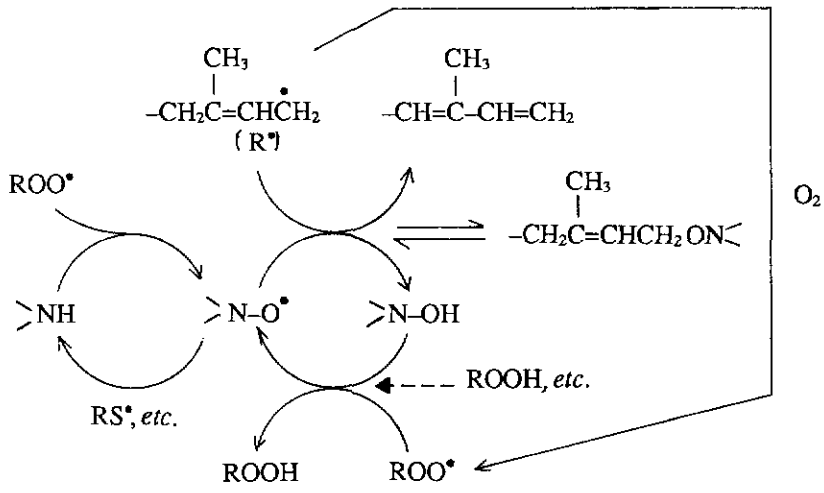


Figure 3. Formation of alkylperoxyl (A) and nitroxyl (B) during the fatiguing of NR in the presence of IPPD.
(After Reference 24)

are interconvertable during fatiguing although not indefinitely so due to side reactions[25]. The cyclical mechanism proposed is summarised in *Scheme 5*.

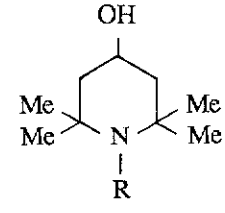


Scheme 5

Oxidation and reduction mechanisms involved in the anti-fatigue activity of aromatic amines (NH)

The analogy to the catalytic mechanism of nitroxyl radicals in polypropylene discussed above is obvious. It should follow from *Scheme 5* that the nitroxyl (>N-O·) and hydroxylamine (>NOH) should be as effective as the parent amine as anti-fatigue agents. *Table 3* compares the activity of some typical aromatic amines and their oxidation products.

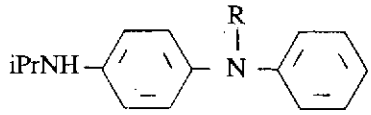
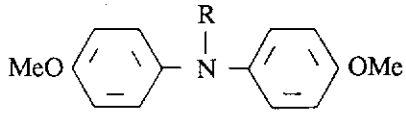
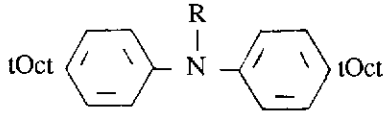
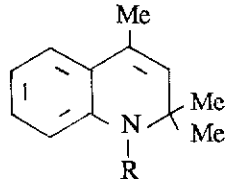
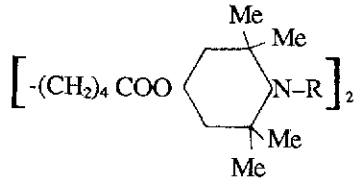
Only nitroxyls and hydroxylamines derived from amines with high anti-fatigue agents were found to be effective anti-fatigue agents themselves and indeed these were more effective than the amines from which they were derived, indicating that side reactions may reduce conversion to anti-fatigue-active agents compared to the nitroxyls themselves. Nevertheless, the reduction of the nitroxyls to the corresponding amines appears to play an essential part in the mechanism of the anti-fatigue activity of the nitroxyls since amines without antioxidant activity (notably XIV, R = H) and their derived nitroxyls (R = O·)



XIV

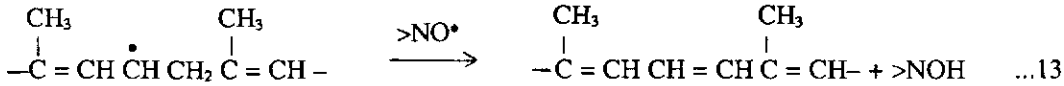
have no significant anti-fatigue activity[26] *(Table 3)* although the nitroxyls are effective mechano-antioxidants in unvulcanised rubber[24]. It was concluded that the sulphur species present in vulcanised rubber reduce the nitroxyls to the corresponding amines which unlike the aromatic amines are not antioxidants and cannot participate in *Scheme 5*.

TABLE 3. FATIGUE LIVES OF NR VULCANISATES CONTAINING AMINES AND THEIR DERIVED OXIDATION PRODUCTS[25,26]

Additive		Fatigue life (h) R = H	O·	OH
	VIII	273	337	–
	XI	207	411	55[a]
	XII	83	88	107
	XIII	53	56	55
		25	30	
Control (no additive)			21	

[a] Insoluble in rubber. Bloomed to the surface.

Oxidation of *cis*-polyisoprenyl radicals by nitroxyl to give unsaturated conjugation *(Reaction 13)* appears to take place even at ambient temperatures[27].



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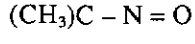
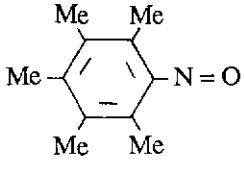
This reaction is driven by the conjugation energy generated by loss of the hydrogen and this reaction is much more facile than that involved in polyolefins where the main reaction at ambient temperatures is believed to be radical pairing.

Spin Traps as Anti-fatigue Agents

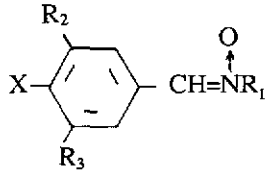
A variety of spin traps, which give rise to nitroxyl radicals in the presence of alkyl radicals, have been found to be effective mechano-antioxidants (processing stabilisers) for polyolefins[15, 28]. Typical are the nitroso-tert-alkanes (e.g. XV), aromatic nitroso compounds (e.g. XVI) and the nitrones (e.g. XVII).



XV

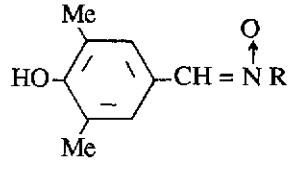


XVI

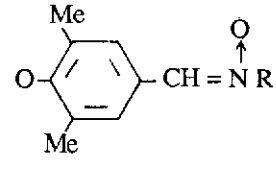


XVII

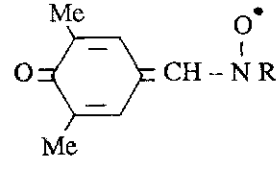
All of them give rise to nitroxyl radicals in polypropylene during processing and it was considered by analogy that they should have anti-fatigue activity in rubbers[15]. Variation of the structure XVII showed that when X = H and R_1 = alkyl, the nitrones are devoid of significant activity. When X = OH, however, significant activity was found although not as high as the 4-alkylaminodiphenyl nitroxyls *(Table 4)*[29]. Although all of the additives in *Table 4* gave nitroxyl radicals during processing in NR, they were not chemically attached to the polymer. This coupled with the lack of anti-fatigue activity of the nitrones without hydroxyl groups suggests that the mechanism of formation of nitroxyl involves oxidation of the phenolic group by alkylperoxyl rather than reduction by alkyl;



XVIII



XIXa

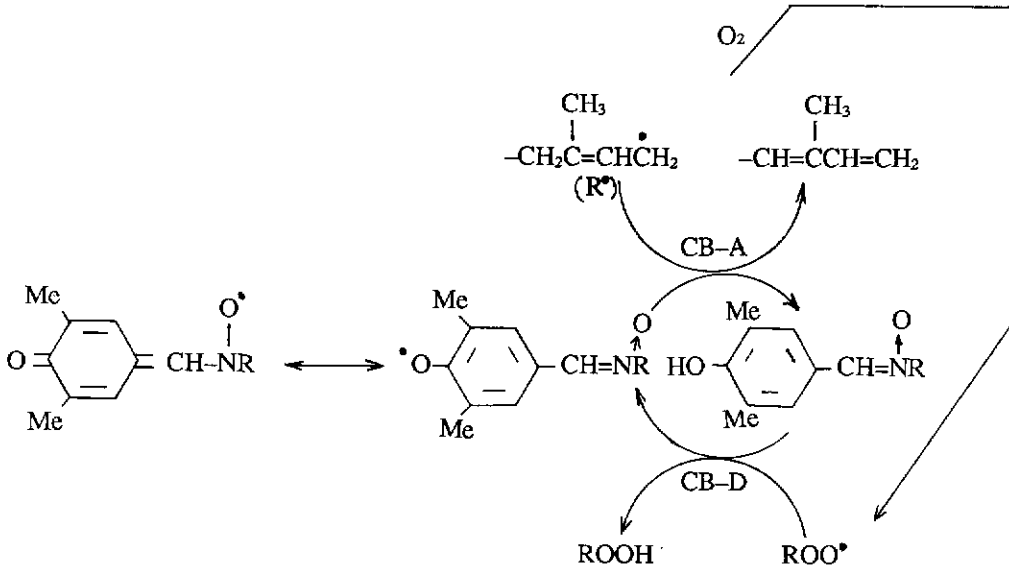


XIXb

TABLE 4. ANTI-FATIGUE ACTIVITY OF BENZALNITRONES (XVII)

XVII				Time to fatigue failure, JIS average (h)
X	R_1	R_2	R_3	
H	tBu	H	H	26
OH	tBu	H	H	30
Cl	iPr	H	H	37
OMe	iPr	H	H	33
OH	tBu	Me	Me	110
OH	iPr	Me	Me	130
OH	Et	Me	Me	93
OH	Me	Me	Me	80
H	Me	H	H	29
IPPD				270
Control				20

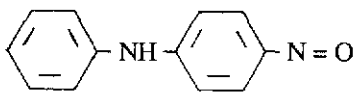
However, no phenoxyl radicals were detected by ESR indicating that the radical produced is more correctly represented by XIXb than XIXa. However, there seems little doubt that the same cyclic mechanism is involved as in the case of the aromatic nitroxyls *(Scheme 6)*[18,29].



Scheme 6

Proposed anti-fatigue mechanism for the 4-hydroxy benzalnitrones (XVIII) in NR[29].

As might be expected, the aliphatic nitroso compounds provide little anti-fatigue activity but the aromatic nitroso compounds are more effective. In particular 4-nitroso-diphenylamine



XX

(XX) has been shown to give a high level of bound nitroxyl under certain conditions and this adduct imparts anti-fatigue activity to NR. Furthermore, it is resistant to solvent extraction or loss by migration from the rubber and under these conditions it is much more effective than IPPD as an anti-fatigue agent.[30].

'Stable' Sulphur Radicals as Anti-fatigue Agents

The ability of sulphur vulcanisates to resist fatigue has been recognised for many years but the reason for this has not so far been clarified. It has been proposed[31,32] that under the influence of strain, S-S cross-links can undergo scission with subsequent recombination and shortening of the polysulphide cross-link. This explanation does not, however, adequately explain the effects of sulphur compounds added to a peroxide vulcanisate[8,18,33]. *Table 5* shows that low molecular weight mono- and disulphides, DLTP and DLPDS are very effective anti-fatigue agents when added to a peroxide vulcanisate[33].

$(C_{12}\ H_{25}\ O\ CO\ CH_2\ CH_2)_2\ S$

DLTP

$(C_{12}\ H_{25}\ O\ CO\ CH_2\ CH_2S)_2$

DLPDS

$(C_{12}\ H_{25}\ O\ CO\ CH_2\ CH_2)_2\ S{-}O$

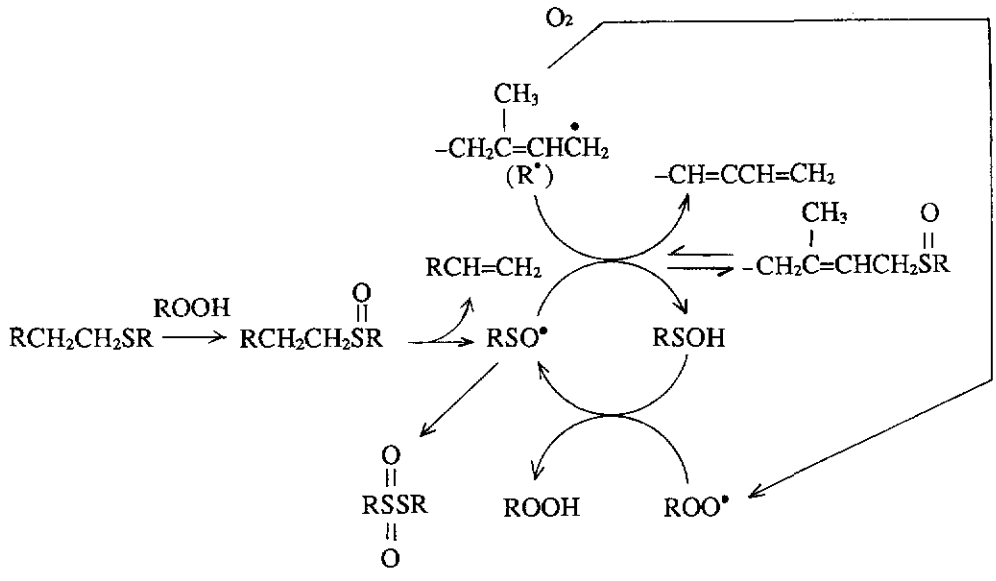
DLSP

The former is oxidised readily by hydroperoxides to the corresponding sulphoxide, DLSP, and then was found to be more effective than DLTP. Sulphoxides are known to be thermally unstable and break down to give sulphinic acids and olefins[34,35]. It seems likely then that alkyl sulphides, whether part of a rubber vulcanisate or added as additives give rise to sulphinyl radicals which are known traps for macro-alkyl radicals[36], thus inhibiting the conventional radical chain reaction *(Scheme 7)*. Although the sulphinyl radical is continuously reformed in *Scheme 7*, the overall process is not very efficient because sulphinyl radicals can disappear in other ways, particularly by

TABLE 5. FATIGUE LIVES OF PEROXIDE CURED NR WITH ADDED SULPHUR COMPOUNDS

Additive concentration (g/100g)	Improvement in fatigue life relative to control (%)		
	DLTP	DLSP	DLPDS
0.5	95	105	133
1.0	127	157	293
2.0	166	209	380

dimerisation to thiosulphinates *(Scheme 7)*. However, in a sulphur vulcanisate there is a large reservoir of sulphides and hence of sulphuryl radicals. They are also formed readily from partially oxidised polysulphides by further oxidation and thermolysis[37].



Scheme 7

Proposed mechanism for fatigue inhibition by sulphur compounds.

CONCLUSION

The concept that some antioxidants could act both as chain-breaking donors and chain breaking acceptors in a catalytic mechanism arose simultaneously in three quite different areas of polymer technology. The idea proved to be seminal and further work has shown the essential unity of the mechanism in the stabilisation of thermoplastics in the melt during processing, in the photo-stabilisation of the thermoplastics and in fatigue prevention in rubbers.

Polymer stabilisation technologists have in the past tended to believe that their own medium is unique and that stabilisation data can rarely be transferred between technologies. The studies reviewed above indicate that, provided certain basic similarities and differences are recognised, of which the most important are oxygen concentration at the site of oxidation and the chemical structure of the substrate, then the common chemistry of catalytic antioxidant action can be transferred across technological boundaries to the ultimate benefit of all polymer technologies[10].

It seems likely then that other examples of the CB-A/CB-D catalytic mechanism will be recognised and exploited in the future in rubbers. The potential application of the mechanism to sulphur vulcanisates has been mentioned in this review, but the possibility of optimising it remains unexplored. It seems likely that the sulphide cross-links found in conventional sulphur vulcanisates are not the ideal structures to give optimum antioxidant activity. A fundamental re-appraisal of the sulphur-accelerator curing system from the standpoint of both heat aging and fatigue could be very beneficial. In the long-term, it may be necessary to consider removing sulphur from

the cross-link altogether and replacing it by sulphur-containing and other antioxidants with catalytic activity in order to independently control the cross-linking and antioxidant processes.

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